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The Solvation of Mercury Ions and the Formation of Their Complexes in Water and Non-aqueous Solvents

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The characteristic features of the formation of mercury complexes in water and non-aqueous solvents are examined. A relation is established between the stability of the complexes and mercury solvates, on the one hand, and the properties of the solvents, on the other. pHg^{2+} mercury complex stability scales have been constructed on the basis of the concept of ionic activities and the possibility of predicting the activities of complex species, the disproportionation constants, and the solubility products of sparingly soluble mercury salts in non-aqueous media has been demonstrated. Correlations for a series of mercury complexes and solvato-complexes and the prospects for the employment of the quantitative characteristics of solvation in the chemistry of mercury complexes are discussed.
The bibliography includes 180 references.

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I. INTRODUCTION

There has been a considerable growth in recent years of the use of non-aqueous solvents as media for a wide variety of synthesis and analytical determinations. Non-aqueous solvents are being used in increasing amounts in industrial chemistry, which necessitates the study of non-aqueous systems. Investigation of the interaction of dissolved substances with the solvent, the most important of which is solvation, is of considerable interest. The determination of the thermodynamic characteristics of solvation makes it possible to predict properties of electrolytes in non-aqueous media (solubility, acidity, stability of complexes, standard potentials, etc.); the knowledge of the solvation characteristics permits a well-founded choice of solvents in the development of rational methods for non-aqueous titrimetry.

The development of the analytical chemistry of non-aqueous solutions follows a path designed to find stable and selective reagents, among which non-aqueous solutions of heavy metal salts, particularly those of mercury, are being used on an increasing scale. The reactions involving the formation of complex and sparingly soluble mercury compounds are widely employed in electrochemistry, analytical chemistry, and chemical engineering.

This review deals with the literature data for the stabilities of mercury complexes in aqueous and non-aqueous solutions published from 1940 until May, 1976: studies dealing with the chemistry of mixed mercury complexes and organomercury compounds are not considered in the review.

The study of the characteristic features of the solvation of mercury ions and the formation of their complexes makes it possible to discover which atoms and groups shows the greatest tendency towards a donor–acceptor interaction with mercury, to establish the nature of the influence of the solvents on the stability of mercury complexes and the solubility of sparingly soluble mercury compounds, and to estimate the degree of solvation of mercury complexes in order to predict their activities in reactions with organic compounds.

II. THE STRUCTURE AND PROPERTIES OF MERCURY ATOMS AND IONS

1. The Electronic Configuration of Mercury and Its Stable Compounds

The outer $6s$ sublevel of the mercury atom contains two electrons; this sublevel is preceded by the filled $5d$ sublevel and the $5f$ sublevel is unfilled. The Hg^{2+} ion is excited as a result of the transfer of one of the $6s$ electrons either to the $5f$ state or the $6p$ state; energetically the $6s^2 \rightarrow 6sp$ excitation is apparently more favourable. The state of the sp valence electrons determines the structure of mercury compounds [1].

It has been suggested that, in the low-temperature radiolysis [2] and low-temperature electrochemical oxidation [3] of mercury compounds, an unstable mercury(III) ion is produced.

Mercury(I) has formally a non-bonding $d^{10}s^1$ configuration, but in reality exists in the form of the dimer Hg_2^{2+}; one of the electrons in the $6s$ orbital is used to form a covalent Hg–Hg bond and the other is used for ionisation. The polyatomic cations Hg_n^{2+} ($n = 3-6$) have been obtained in reactions in melts and in liquid sulphur dioxide [4].

The Hg_2^{2+} ions exhibit a distinct tendency towards the formation of sparingly soluble compounds. The best known are mercury (I) halides; the fluoride hydrolyses in water, while the remaining mercury(I) halides are sparingly soluble. Mercury(I) perchlorate, sulphate, chlorate, bromate, and iodate are moderately soluble. The soluble mercury(I) salts are associated: their stability constants are as follows: $20(Hg_2SO_4)$; $250[Hg_2(SO_4)_2^{2-}]$; $0.9(Hg_2ClO_4^+)$ (Infeld and Sillén [5]); $1.05[Hg_2(NO_3)_2]$; $0.5(Hg_2NO_3^+)$ (Corbett [6]).

The small amount of data concerning mercury(I) complexes is associated with the weak tendency of Hg_2^{2+} towards the formation of coordinate bonds and with its disproportionation; the latter process takes place particularly vigorously in the presence of ligands forming stable mercury(II) complexes. Mercury(I) complexes can be obtained by introducing into the solution ligands which react to form

ionic bonds: oxalate, succinate, pyrophosphate, and triphosphate[7]. Aniline[8], phenanthroline[9], trifluorophosphine[10], diacetohydrazide[11], and triethanolamine[12] complexes of mercury(I) are known. The dimeric structure of mercury(I) persists in its complexes with arenes; in complexes with *m*-dinitrobenzene a bidentate coordination of NO_2 groups to Hg_2^{2+} was observed[13]. Mercury(I) complexes have one and more, rarely two, ligand molecules[10,14]. Only a few of the complexes—$Hg_2[Ph_3PO]_4(ClO_4)_2$ and $Hg_2[PhNO]_4(ClO_4)_2$—contain four ligand molecules[15].

The highly dissociated mercury(II) salts (perchlorate, nitrate, and sulphate) exhibit ionic properties; the association constants of $Hg(NO_3)_2.0.5H_2O$ are 1.28 (K_1) and 1.0 (K_2).[5] In contrast to the fluorides, the Hg–Hal bond in other halides is covalent. Like the halides, mercury(II) cyanide, oxalate, acetate, thiocyanate, and phosphate are partly or completely dissociated in water. Mercury(II) ions form a considerable number of complex compounds whose stability is characterised below.

The Stability of Aquo- and Solvato-Complexes of Mercury

Mercury ions exist in aqueous solutions in the form of diaquo-ions having the linear structure $Hg(H_2O)_2^{2+}$. The diaquo-complexes can be converted into coordination-saturated tetra-aquo- or even hexa-aquo ions[16]. The thermodynamic functions for the formation of hydrated mercury ions[17,18] are listed below:

	ΔG^0, kcal mole^{-1}	ΔH^0, kcal mole^{-1}	ΔS^0, e.u. (298 K)
Hg^{2+} (aq)	39.365 ± 0.025	40.67 ± 0.050	−8.66 ± 0.20
Hg_2^{2+} (aq)	36.713 ± 0.025	39.87 ± 0.050	15.72 ± 0.20

The enthalpy, energy, and entropy of hydration of the mercury(II) ion at infinite dilution are respectively $-\Delta H_h$ = 443 kcal g-ion^{-1}, $-\Delta G_h$ = 431 kcal g-ion^{-1}, and $-\Delta S_h$ = 40.9 e.u.[19]

The formation of aquo-complexes is complicated by the fact that the metal ion interacts vigorously with one of the ionic forms of the solvent. Mercury(II) hydroxide is an extremely weak base ($K_{diss} = 1.8 \times 10^{-22}$),[20] which exhibits amphoteric properties; this explains the appreciable influence of pH on the state of mercury salts in solution[21]. Thus mercury(II) chloride exists in solution as $HgCl_2$ at pH < 3, undergoes partial hydrolysis at pH 5–7, and at pH > 7 the entire mercury in solution is present as $Hg(OH)_2$.[22] The successive dissociation of hydrate complexes treated as diaquo-acids is characterised by the following negative logarithms of the equilibrium constants for mercury(II): $pk_1 = 2.8$ and $pk_2 = 3.5$;[23,24] for the diaquo-complex of mercury(I), $pk_1 = 4.0$–4.6.[25] The hydrolytic cleavage of mercury salts takes place in any proton-donating solvent; for mercury(II) perchlorate, the corresponding reactions

$$Hg^{2+} + H_2O \overset{k_1}{\rightarrow} HgOH^+ + H^+$$

$$Hg^{2+} + 2H_2O \overset{k_2}{\rightarrow} Hg(OH)_2 + 2H^+$$

are characterised by the constants $pk_1 = 3.70$ and $pk_2 = 6.30$.[26]

The formation of solvato-complexes of mercury is associated with the solvation of all the species involved in the reaction. Solvents (Solv) with appreciable electron-donating properties behave as competing ligands in relation to water[27] and are capable of displacing it from the inner coordination sphere of mercury aquo-ions:

$$[Hg_n(H_2O)_m]^{2+} + l\,Solv \rightleftarrows [Hg_n(Solv)_l(H_2O)_{m-l}]^{2+} + l\,H_2O\,.$$

This process can proceed up to the formation of solvato-complexes having the limiting coordination $[Hg_n(Solv)_m]^{2+}$. A comparative estimate of the stability of solvato-complexes can be made by employing the activity coefficients for the transfer of the corresponding ions; this quantity, designated by[28] $\gamma_t(M^{Z+})$ in accordance with an IUPAC recommendation, characterises the free energy ΔG of the transfer of the M^{Z+} ion from the standard solvent (usually an aqueous solution with unit activity of M^{Z+}) to the test solvent Solv:

$$-\Delta G = RT(\ln K_{[M(Solv)_m]^{z+}} - \ln K_{[M(H_2O)_m]^{z+}}) =$$

$$= zF({}^{H_2O}E^0_{M^{z+}/M} - {}^{Solv}E^0_{M^{z+}/M}) = RT \ln \gamma_t(M^{z+}).$$

Table 1. The negative logarithms of the activity coefficients for the transfer of mercury(I) and mercury(II) ions from water to non-aqueous solvents (25°C).

Solvent	$p\gamma_t(Hg_n^{2+})$		Conditions of measurements		Method	Refs.
	Hg^{2+}	Hg_2^{2+}	Reference electrodes*	Ionic strength		
Methanol (MeOH)	1.7	2.1	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
	3.6	3.8	n.h.e.(H_2O)	0 **	potent.	31
	3.7	3.9		0	spectr.	31
Ethanol (EtOH)	2.8	3.1	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
	4.3	4.6	n.h.e.(H_2O)	0 *	potent.	30
	4.2	4.3	—	0	spectr.	31
Propanol (PrOH)	3.1	4.8	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
	4.8	5.0	n.h.e.(H_2O	0 **	potent.	30
	4.6	5.1	—	0	spectr.	31
Butanol (BuOH)	5.2	5.4	n.h.e.(H_2O)	0 **	potent.	30
	5.2	5.3	—	0	spectr.	31
Pentanol (AmOH)	5.9	6.3	n.h.e.(H_2O)	0 **	potent.	30
	5.4	6.5	—	0	spectr.	31
Hexanol (HexOH)	5.4	5.8	—	0	spectr.	31
Heptanol (HeptOH)	5.5	6.0	—	0	spectr.	31
Ethylene glycol (EG)	−6.8	−5.6	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	32
	−6.9	−3.5	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Propylene carbonate (PC)	—	3.4	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	33
	2.8	1.0	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Acetonitrile (AN)	4.0	3.4	n.h.e.(H_2O)	0.1 (Et_4NClO_4)	potent.	34
	9.0	8.4	n.h.e.(H_2O)	0.1 (Et_4NClO_4)	potent.	35
	3.1	9.0	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Dimethyl sulphoxide (DMSO)	−13.9	−15.2	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	36
	−11.8	−8.6	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Dimethylformamide (DMF)	−12.4	−11.0	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	37–39
	−10.3	−7.6	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Dimethylacetamide (DMA)	−12.4	−11.0	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	39
Hydrazine (Hy)	—	−7.1	Rb+/Rb	0.1 (Et_4NClO_4)	potent.	40
Pyridine (P)	−24.8	—	Fc+/Fc	0.2 ($LiClO_4$)	potent.	41
Pyrrolidone (Pn)	−14.4	−11.8	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	42
N-Methylpyrrolidone (N-MP)	−14.7	−12.5	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	43
N-Methylacetamide (N-MA) (30°C)	−9.2	—	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	44
Acetone (Ac)	1.4	1.0	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Nitromethane (NM)	—	8.5	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	45
	4.5	6.9	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Acetic acid (AcOH)	—	−5.2	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	46
	3.8	5.2	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29

*Notation: n.h.e. = normal hydrogen electrode; Fc^+/Fc = ferrocene/ferrocenium electrode; Rb^+/Rb = rubidium reference electrode.

**Extrapolation to infinite dilution.

Here $K_{[M(Solv)_m]^{Z+}}$ and $K_{[M(H_2O)_m]^{Z+}}$ are the stability constants of the solvato- and aquo-complexes of the ion M^{Z+} respectively, ${}^{H_2O}E^0_{M^{Z+}/M}$ and ${}^{Solv}E^0_{M^{Z+}/M}$ are the standard potentials of the M^{Z+}/M system in water and the non-aqueous solvent Solv respectively, and F is the Faraday. Thus the quantity $RT \ln \gamma_t(M^{Z+})$ represents the difference between the standard chemical potentials of the ion M^{Z+} in two different solvents.

The activity coefficients for the transfer of mercury(I) and mercury(II) ions from water to non-aqueous solvents of different types have been found[29–46] from electrochemical

and spectroscopic measurements and are listed in Table 1; the polarographic measurements have been carried out using a Strehlow ferrocene/ferrocenium reference electrode[47], the potentiometric measurements were carried out using hydrogen and rubidium reference electrodes, and spectrophotometric measurements were performed using calculations by the Asmus method. The donor–acceptor properties of solvents in relation to a particular ion are characterised by the stability of the corresponding solvato-complexes; such data for mercury(II) solvato-complexes[31] are presented in Table 2.

Table 2. The stabilities of mercury solvato-complexes with organic solvents at 25°C (according to ultra-violet spectroscopic data)[31].

Mercury salt	$\lg K_{st}$ in different solvents*									
	H_2O	MeOH	EtOH	PrOH	BuOH	AmOH	GsOH	GpOH	AcOH	AH
$Hg(ClO_4)_2$	2.6	−1.09	−1.61	−2.01	−2.59	−2.77	−2.80	−2.85	−1.71	−2.01
$Hg_2(NO_3)_2$	—	−0.75	−1.10	−1.29	—	—	—	—	−1.88	−0.48

*The designations of the solvents are the same as in Table 1.

In alcohols the solvation energy of mercury ions decreases compared with water; aliphatic monohydric alcohols are weak electron donors in relation to Pearson's "soft" acids[48]. Thus ΔG for the transfer of $HgCl_2$ from water to ethanol is −1.623 kcal mole^{-1} [49] according to solubility data[49].

Acetonitrile, nitromethane (and probably also sulpholane) constitutes a group of solvents whose dielectric constants and solvating capacities are high, while their electron-donating forces in relation to cations are weak (in the absence of specific interactions). In consequence of the weaker solvation of mercury ions, the mercurimetric oxidation of dihydroxybenzenes[50] and inorganic cations[51] as well as electrophilic addition of mercury(II) salts to unsaturated hydrocarbons[52–54] proceed faster in alcohols and acetic and trifluoroacetic acids. The specific interaction of mercury ions with dipolar aprotic solvents leads to the formation of stable solvato-complexes of mercury(I) and mercury(II) with dimethyl sulphoxide, dimethylformamide, dimethylacetamide, pyrrolidinone, and *N*-methylpyrrolidinone. The complexes with dimethyl sulphoxide are particularly stable: the solvent molecules have two electron-donating centres. The formula $3HgCl_2.2Solv$, with coordination via oxygen, has been attributed[55] to mercury(II) chloride complexes with sulphoxides. There is a possibility[56] of the coordination of mercury(II) nitrate to acetonitrile; the coordination number was found to be 3.5.[57] The hydrolysis of acetonitrile under the influence of traces of water in a solvent, catalysed by mercury(II) salts, proceeds with formation of acetamide complexes of mercury; in contrast to transition metal complexes, the latter involve coordination via the nitrogen atom[58,59].

The polarographic data presented in Table 1 were obtained on the hypothesis that $E_{1/2} \simeq E^0$; although the formal electrode potentials, measured in the presence of supporting electrolytes, do not reflect directly the changes in the free energy of formation of ions, they nevertheless give an idea about the solvating capacity of solvents. (Comparison of the half-wave potentials and the activity coefficients calculated with their aid is justified when the measurements are performed in identical supporting electrolyte solutions and when the same working hypothesis is used.)

Table 3. The electrode potentials of the Hg^{2+}–Hg_2^{2+}–Hg^0 system (at 25°C)*.

Solvent	Process potential, V			Conditions of measurements		Refs.
	$Hg^{2+}\rightarrow Hg_2^{2+}$	$Hg_2^{2+}\rightarrow Hg^0$	$Hg^{2+}\rightarrow Hg^0$	Reference electrode	Ionic strength	
H_2O	0.907	0.792	0.850	n.h.e.(H_2O)	0	62,63
H_2O	—	—	2.48	Rb^+/Rb	0	60
H_2O	—	0.390	0.450	Fc^+/Fc	0.1 (Et_4NClO_4)	64
H_2O	—	0.430	0.460	Fc^+/Fc	1.0 ($LiClO_4$)	65,66
MeOH	—	0.764	—	n.h.e.(H_2O)	0	67
MeOH	—	0.490	0.510	Fc^+/Fc	1.0 ($LiClO_4$)	65
MeOH	—	0.740	—	n.h.e.(MeOH)	0	68
EtOH	—	0.760	0.739	n.h.e.(EtOH)	0	69
EtOH	—	0.520	0.540	Fc^+/Fc	1.0 ($LiClO_4$)	65
EG	—	0.220	0.245	Fc^+/Fc	0.1 (Et_4NClO_4)	64
EG		0.330	0.240	Fc^+/Fc	1.0 ($LiClO_4$)	65
Pn	—	0.035	0.015	Fc^+/Fc	0.1 (Et_4NClO_4)	70
N-MP	0.021	0.029	0.025	Fc^+/Fc	0.1 ($LiClO_4$)	43,71
Hy	—	0.770	—	Fc^+/Fc	0	28
Hy	—	2.880	—	n.h.e.(Hy)	0	73
DMF	—	0.079	0.090	Hg/Hg_x^{2+}	0.1 (Et_4NClO_4)	38
DMF	—	0.160	0.210	Fc^+/Fc	1.0 ($LiClO_4$)	65
DMF	0.100	0.058	—	Fc^+/Fc	0.1 (Et_4NClO_4)	74,75
DMF	—	—	0.90	BBCr (I)	0.1 (Et_4NClO_4)	76
DMA	0.110	0.070	0.090	Fc^+/Fc	0.1 (Et_4NClO_4)	71
PN	—	—	2.56	Rb^+/Rb	0.1 (Et_4NClO_4)	60
BN	—	—	2.58	Rb^+/Rb	0.1 (Et_4NClO_4)	60
BN	1.45	1.25	—	BBCr (I)	0.1 (Et_4NClO_4)	76
iso-BN	—	—	2.55	Rb^+/Rb	0.1 (Et_4NClO_4)	60
AN	—	0.482	0.490	Fc^+/Fc	0.1 ($LiClO_4$)	77
AN	—	—	0.993	n.h.e.(H_2O)	0	68
AN	—	0.250	—	n.h.e.(AN)	0	68
AN	0.7	0.5	—	sat.c.e.	0.1 ($NaNO_3$)	78
AN	—	0.690	0.550	Fc^+/Fc	1.0 ($LiClO_4$)	65
AN	—	—	2.58	Rb^+/Rb	0.1 (Et_4NClO_4)	60
AN	1.4	1.2	—	BBCr (I)	0.1 (Et_4NClO_4)	76
PC	0.150	0.495	—	Fc^+/Fc	0.1 (Et_4NClO_4)	79
PC	—	0.460	0.540	Fc^+/Fc	1.0 ($LiClO_4$)	65
PC	—	—	1.33	BBCr (I)	0.1 (Et_4NClO_4)	76
DMSO	0.882	0.684	0.783	n.h.e.(DMSO)	0.1 (Et_4NClO_4)	80
DMSO	—	—	0.80	BBCr (I)	0.1 (Et_4NClO_4)	76
DMSO	—	0.17	0.12	Fc^+/Fc	1.0 ($LiClO_4$)	65
Ac	—	0.716	—	n.h.e.(H_2O)	0	67
Ac	—	—	2.65	Rb^+/Rb	0.1 (Et_4NClO_4)	76
Ac	—	0.46	0.50	Fc^+/Fc	1.0 ($LiClO_4$)	65
NM	—	0.640	—	Fc^+/Fc	0.1 (Et_4NClO_4)	45
NM	—	0.63	0.59	Fc^+/Fc	1.0 ($LiClO_4$)	65
NB	—	—	0.14	BBCr (I)	0.1 (Et_4NClO_4)	76
HCOOH	—	0.180	—	n.h.e.(HCOOH)	0	68
AcOH	—	0.240	—	Fc^+/Fc	0.1 (Et_4NClO_4)	46
AcOH	—	0.58	0.57	Fc^+/Fc	1.0 $(LiClO)_4$	65
P	—	—	0.180	$Ag/AgClO_4$	0.2 ($LiClO_4$)	41
P-H_2O						
10 wt.% P	—	0.230	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
20 wt.% P	—	0.227	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
40 wt.% P	—	0.249	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
60 wt.% P	—	0.264	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
80 wt.% P	—	0.264	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
EtOH-H_2O 10 wt.% EtOH	0.591	—	—	n.h.e.(EtOH)	0	69
70 wt.% EtOH	0.723	—	—	n.h.e.(EtOH)	0	69

*Notation: PN = propionitrile; BN = butyronitrile; iso-BN = isobutyronitrile; NB = nitrobenzene; BBCr(I) = bisbiphenylchromium(I) iodide reference electrode.

According to the anodic dissolution potentials for mercury[60], the solvation energy of mercury(I) ions and the stability of mercury(I) perchlorate in water are higher than in acetone or acetonitrile; in aromatic nitriles the solvation energy of mercury ions is greatly reduced compared with water. The decrease of the solvating capacity of solvents in relation to mercury ions proceeds in the

following sequence: dimethyl sulphoxide > *N*-methylpyrrolidinone > pyrrolidinone > dimethylformamide, dimethylacetamide > ethylene glycol > water > acetone > methanol > ethanol > propylene carbonate > propanol > acetic acid > nitromethane > acetonitrile.

3. Disproportionation and Standard Potentials of Mercury Systems

The energies of the mercury(I) disproportionation reactions are low; thus $\Delta H = 8$ kcal mole^{-1} and $\Delta G = 6.3$ kcal mole^{-1} for the reaction[81]

$$Hg_2Cl_2 \rightleftarrows HgCl_2 + Hg \cdot$$

It is possible to determine K_d indirectly via the standard potentials:

$$pK_d = \frac{E^0_{Hg^{2+}/Hg^0} - E^0_{Hg_2^{2+}/Hg^0}}{2.3RT/zF}, \quad (1)$$

where z is the number of electrons. The literature data for the standard and half-wave potentials of mercury systems are presented in Table 3 and the values of pK_d calculated by Eqn. (1) are in Table 4.

Table 4. The negative logarithms of the disproportionation constants of mercury(I) ions calculated from the values of E° on the ferrocene scale.

Solvent	pK_d	References	Solvent	pK_d	References
H_2O	2.07	62	PC	2.76	65
H_2O	2.22	63	DMF	0.70±0.25	74
H_2O	1.14	65	DMF	−1.38	65
MeOH	0.69	65	DMA	0.60±0.25	39
EtOH	0.69	65	NM	−1.38	65
PrOH	−1.03	65	Ac	1.38	65
EG	−3.10	65	AcOH	−0.35	65
EG	0.85±0.25	72	DMSO	3.4	80
Pn	−0.69	42	DMSO	1.6	82
N-MP	−0.14±0.09	71	DMSO	−1.71	65
N-MP	−0.1±0.1	70	AN	2.7±2	77

Although comparison of the potentials measured on different scales is in fact difficult, it is nevertheless evident that the potentials of the mercury systems are more negative in dimethyl sulphoxide, dimethylformamide, dimethylacetamide, *N*-methylpyrrolidinone, and ethylene glycol than in water. The literature data[46] for acetic acid are probably erroneous; this solvent causes only slight solvation of inorganic cations[28]. Acetonitrile, propylene carbonate, and nitromethane weakly solvate mercury ions; in these solvents the oxidising properties of mercury ions should be manifested to a greater extent.

The values of K_d (Table 4) have been determined in many instances with a considerable error; nevertheless one can note that Hg_2^{2+} ions are stable in water (disproportionation takes place to the extent of 1%), propylene carbonate, and an acetic anhydride–acetic acid mixture (disproportionation to the extent of 5%).[83] The disproportionation of Hg_2^{2+} takes place partly in *N*-methylpyrrolidinone, dimethylformamide, and dimethylacetamide and almost wholly in ethanolamine[84], ethylenediamine, and *N*-methylacetamide[86].

Any significant weakening of the Hg–Hg bond promotes the disproportionation reaction; reagents which decrease the activity of Hg^{2+} as a result of the formation of complex or sparingly soluble mercury(II) compounds favour disproportionation.

It is to be expected that the solvation of both valence forms contributes to the change in the disproportionation constants; indeed, since

$$K_d = a_{Hg^{2+}}/a_{Hg_2^{2+}}$$

$$\text{and } K_d^{Solv} = K_d^{H_2O} \frac{\gamma_t(Hg^{2+})}{\gamma_t(Hg_2^{2+})},$$

one can write

$$pK_d^{Solv} = pK_d^{H_2O} + p\gamma_t(Hg^{2+}) - p\gamma_t(Hg_2^{2+}).$$

In a real process disproportionation of a sparingly soluble mercury(I) salt (in electrodes of the second kind, for example) is associated with the stability of the complexes formed in the reaction; for the reaction

$$Hg_2L_2 + mL^- \overset{K'_d}{\rightleftarrows} [HgL_{m+2}]^{m-} + Hg, \quad (2)$$

the negative logarithm of the disproportionation constant is

$$pK'_d = pK_d + pSP_{Hg_2L_2} + pK_{[HgL_{m+2}]^{m-}},$$

where $SP_{Hg_2L_2}$ is the solubility product of the salt undergoing disproportionation.

The change in the values of pK'_d on passing from water to the non-aqueous solvent Solv is associated with the nature of the solvation of all the compounds involved in equilibrium (2):

$$(pK'_d)^{Solv} = (pK'_d)^{H_2O} + p\gamma_t([HgL_{m+2}]^{m-}) - m \cdot p\gamma_t(L^-). \quad (3)$$

III. CHARACTERISTIC FEATURES OF THE FORMATION OF MERCURY(II) COMPLEXES IN WATER

1. The Electronic Structure of Mercury Complexes

The characteristic coordination numbers n of mercury(II) are 2 and 4; however, complexes with $n = 5$ are known[87]. The formation of octahedral complexes[88] is less typical; for example, hexa-aquo-complexes of mercury perchlorate are formed in water only at low salt concentrations[89]; an increase of the concentration leads to the formation of tetra-aquo-complexes.

Donor–acceptor complexes of mercury are formed as a result of the supply by the ligand electron-donor atom of a lone electron pair to an acceptor s or p orbital of mercury(II). The donor electrons fill the unoccupied s and p sublevels of the external level and form hybrid sp^3 orbitals; furthermore, the ligand itself can behave as an acceptor in relation to the electrons of the $5d$ sublevel of mercury.

Since the $5d$ sublevel is filled, stabilisation by the ligand field is not characteristic of mercury complexes; the stereochemistry of the complexes is determined exclusively by ion size, electrostatic forces, and the covalence of the bonds. The high stability of the mercury complexes has been explained[90] by the employment of the hybrid sp^3 orbitals of the metal and of the most stable tetrahedral configuration in coordination.

2. The Properties of Ligands and the Stability of Complexes

Mercury(II) is classified[91] as a typical representative of "soft" acids, the sequence of the changes in the stability of the complex species being identified with the sequence in the changes in the metal–ligand bond strength. Mercury ions form stronger complexes with the majority of ligands than other *d* elements; this applies to both acido-complexes and to ammines and complexonates. The stability of the complexes is determined to some extent by the nature of the polarisation of the ligands; the increase of the polarisability of the ligands in the series $Cl^- < Br^- < I^-$ (decrease of electron affinity[92]) is combined with an increase in the same sequence of the tendency of the ligands towards the formation of π bonds and with increase in stability of the complexes[62]. This sequence of the changes in the stability of mercury halide complexes indicates an appreciable role of the enthalpy component in complex formation[93].

A remarkable feature of the stereochemistry of mercury chloro-complexes is a tendency towards the retention of the linearity of the Cl–Hg–Cl group. The free energy of formation ΔG (kcal mole^{-1}) of hydrated complex ions varies as follows for halide[94-98] and cyanide[97,99] complexes: 22.1($HgCl_4^{2-}$); 29.5($HgBr_4^{2-}$); 41.3(HgI_4^{2-}); 54.8[$Hg(CN)_4^{2-}$]. The increased stability of the mercury cyanide complex is accounted for by the greater strength of the Hg–CN bond compared with Hg–Hal.[97]

The increase in the stability of the complexes is associated with the formation of a donor π bond[100]; correspondingly, complexes with electron-donating sulphur, selenium, and phosphorus atoms [$S{=}C(NH_2)_2$, $Se{=}C(NH_2)_2$, $HO(CH_2)_2$–S–$(CH_2)_2$–NH_2, Ph_2–$PC_6H_4SO_3^-$, and $HO(CH_2)_2PEt_2$] are extremely stable[101,102]. This also applies to mercury sulphide[103], thiocyanate[104], and selenocyanate[105] complexes.

A relatively low stability is characteristic of mercury complexes with "hard" ligands (Hal^-, NR_3, NH_3, N_3^-, OH^-, SO_4^{2-}, NO_2^-, NO_3^-, and $RCOO^-$); the formation of a donor–acceptor σ bond predominates in this case[101,106-108].

A decrease of the strength of the Hg–L bond in the series Se > S > N > O is characteristic of atoms with filled *d* orbitals, which are capable of forming $d_\pi - d_\pi$ bonds with atoms having vacant *d* orbitals[90]. The stability of amino-complexes exceeds that of carboxylate complexes approximately by 10 orders of magnitude; the Hg–N bond is 2–2.5 times stronger than the Hg–O and Hg–C bonds (the free energy of the latter is 24–36 kcal mole^{-1} [109]).

Mercury complexes with carboxylic acids[110-118] and hydroxyacids[113-115] usually have the 1 : 1 (rarely 1 : 2) composition and are characterised by a certain stability ($\lg K_{st} \leq 8$). The replacement of an oxygen atom in the ligand molecule by sulphur entails a sharp increase in the stability of the complexes, which is characteristic of thiocarboxylates[119-122] and unithiol derivatives[123,124].

The basicity of the nitrogen atom and the stability of complexes. The stability of the donor–acceptor bond between nitrogen and mercury atoms is determined by the density of the electron cloud at the nitrogen atom. The stability of mercury complexes with nitrogen-containing ligands is higher the greater the basicity of the ligands; this relation is maintained for ligands of different types[125-127] and can be represented by the following equations:

$$\lg K_{HgL} = 1.08\, p K_{HL} - 0.53 \text{ (ammines)};$$

$$\lg K_{HgL} = 0.91\, p K_{HL} + 1.81 \text{ (barbiturates)};$$

$$\lg K_{HgL} = 1.25\, p K_{HL} + 1.48 \text{ (sulphamides)};$$

$$\lg K_{HgL} = 0.73\, p K_{HL} + 1.01 \text{ (hydroxypyridines and hydroxypyrimidines)}.$$

Steric hindrance and the presence in ligands of functional groups capable of interacting with mercury(II) cause a deviation of plots of $\lg K_{HgL}$ from linearity. Analogous relations are characteristic also of mercury complexonates. The slope of these lines usually depends[128] on the ionisation potential of the central atom and the polarisation of the ligands by the metal ion. Such relations for aliphatic ammines have slopes close to unity; with intensification of the capacity of the metal ion for the formation of d_π bonds and with increase of the degree of stabilisation in the ligand field, the slopes increase. The linearity of these relations holds only for a series of ligands which are mutually similar structurally, form the same number of chelate rings, and have the same capacity for the formation of π bonds.

Pyrimidine derivatives interact with mercury(II) ions in three possible ways: by the coordination of the carbonyl oxygen of the mercury salt with the neutral ligand; by electrophilic attack with displacement of a proton and the formation of an Hg–C bond; by electrophilic attack with formation of an N–Hg bond[129]. Alkylamines[130-133], π-electron systems (pyridine[132] and aniline[134]), and amino-acids[135-137] bind mercury ions more weakly than other nitrogen-containing ligands (purines and pyrimidines, and imidazole).

Cyclisation and the stability of the complexes. The presence of three five-membered rings in the mercury(II) complex of EDTA is responsible for the highest stability of the complex[138]. Mercury complexes of triethylenediaminetetra-acetic[139], cyclohexane-1,2-diaminetetra-acetic[140], diethylenetriaminepenta-acetic[141], and triethylenetetraminehexa-acetic[142] acids have similar structures. The enhancement of the basic properties of these ligands compared with EDTA stabilises the mercury complexes.

The stability of mercury compounds with complexones having the general formula $(HOOCCH)_2$–$(CH_2)_x$–$(CH_2COOH)_2$ varies non-linearly with increasing x, reaching a minimum for six-membered rings ($x = 3$). A further increase of x leads to the stabilisation of the complexonates: with increase in the size of the ring, its strain, due to the bending of the *sp* orbitals of the mercury ion, diminishes[90].

Complexes with nitrilotriacetate[115], ethylenediaminedimalonic, ethylenediaminedisuccinic, and ethylenediaminediglutaric acids[142], propylenediaminetetra-acetic acid[143], dimethylethylenediaminetetra-acetic acid[140], ethylene disulphide diacetic acid[144] [data for this ligand are not in this reference (Ed. of Translation)], and other complexones[145,146] have low stability constants ($\lg K_{st} \leq 17$). Introduction of sulphur into the complexone molecule leads to a marked stabilisation of phthalyltetrathioacetic acid complexes: $\lg K_{st}[Hg(OH)_2L] = 45$.[147]

Olefin complexes. Many olefin reactions proceed via the formation of intermediate compounds of olefins with mercury atoms; the highest strength of the mercury–olefin bond is due to the involvement of both σ-donor and π-acceptor orbitals in complex formation. The activation of olefins by complexes of mercury and other metals[148] leads to the loosening and a decrease of the multiplicity of

the C=C bond and also to an increase of the positive charge on the carbon atoms owing to the formation of a three-membered ring in which the metal ion plays the role of a heteroatom. The stability constants of the ethylene, propene, and cyclohexene complexes of mercury are [149,150] respectively 1.4×10^4, 1.9×10^4, and 2.2×10^4.

IV. MERCURY COMPLEXES IN MIXED AND NON-AQUEOUS SOLVENTS

1. The Properties of the Solvents and the Stability of the Complexes

The formation of mercury complexes in non-aqueous solvents is determined by the nature of the solvation of mercury ions and the ligands: the stability of the complex species $[HgL_n]^{(2-nl)+}$ is greater than that of the solvato-complexes $[Hg(Solv)_m]^{2+}$ and $[L(Solv)_p]^{l-}$, and the ligands L^{l-} displace solvent molecules more or less readily from the inner coordination sphere of the solvato-complex of mercury:

$$[Hg(Solv)_m]^{2+} + n[L(Solv)_p]^{l-} \rightleftarrows [HgL_n]^{(2-nl)+} + (m + np)\,Solv \quad .$$

Otherwise the stability of the complexes $[HgL_n]^{(2-nl)+}$ is low. In the majority of mixed solvents the influence of the organic cosolvent on the stability of the complexes can be accounted for from the electrostatic standpoints described by the Born equation; indeed the relation between $\lg K$ and $1/\epsilon$ is linear for mercury halide, thiocyanate, and cyanide complexes in aqueous pyridine solutions [81], for cyanide complexes in water–ethanolamine and water–ethylenediamine mixtures [86], and for chloride complexes in aqueous methanol [151], ethanolamine, and ethanol [152] mixtures. The absence of such linearity for the *N*-methylacetamide–dimethylformamide system has been explained [44] by the appreciable electron-donating properties of *N*-methylacetamide in relation to mercury(II): the specific interaction of mercury ions with the solvent can make a significant contribution to the change in the stability of the complex when the composition of the medium is altered.

The introduction of donor-active solvents into aqueous solutions weakens hydration and increases the coordination number to $n > 4$. On the other hand, in pure non-aqueous solvents the solvation of ions can reduce their coordination capacity. Thus in aqueous methanol (up to 10 M MeOH) and aqueous ethanol (9 M EtOH) mixtures mercury thiocyanate complexes $[Hg(SCN)_n]^{(2-n)+}$ with $n = 5$ are formed, whereas in aqueous acetone (10M acetone) n is actually 6; [158] in pure ethanol and acetone n usually does not exceed 4. Similarly, in the formation of acetate complexes in water and methanol n does not exceed 3, while in ethanol and ethylene glycol n decreases to 2. [111,112]

The literature data on the stability of mercury complexes in non-aqueous solvents are numerous: they are available for halide and cyanide complexes in methanol [153-155], ethanol [152-154], acetone [153,154], ethylene glycol [156], pyrrolidone [43], *N*-methylpyrrolidone [70,71], dimethylformamide [39,72,154,157-161], dimethylacetamide [39,162], *N*-methylacetamide [44], ethylenediamine [85], ethanolamine [152], pyridine [41], liquid ammonia [163], acetonitrile [35,164-168], and dimethylsulphoxide [79,82,158-160]. The high stability of mono- and di-ethanolamine complexes of mercury in ethanol [152] and the dithizone, thiourea, and thioacetate complexes in dimethylformamide [39,169] has been noted.

The appreciable solvation of heavy metal ions in aprotic dipolar solvents [28,170] should have entailed a decrease of the stability of the mercury complexes in these media compared with their stability in water. Assuming that the electron-donating characteristics of dimethylsulphoxide, dimethylformamide, and dimethylacetamide are virtually the same, equal stabilities of the complexes in these solvents would be expected. However, the stability of the complexes is apparently determined not so much by the donor number (although the formation of the complexes is undoubtedly facilitated by a decrease of the donor numbers of the medium [172]) and the dielectric constant as by the solvation energies of the anions (ligands and complex species). The weak solvation of anions in aprotic dipolar solvents [173] leads to an increase of the stability of the coordination iodo-complexes in these media by 1–5 orders of magnitude and of the chloro- and bromo-complexes by 10–15 orders of magnitude compared with the stability of the same species in water. In aqueous solutions the stability of mercury complexes increases in the sequence $HgCl_2 < HgCl_4^{2-} < Hg(SCN)_2$, $HgBr_2 < HgBr_4^{2-} < HgI_2 < HgI_4^{2-}$. This series changes for aprotic dipolar solvents [4]; for example, in dimethyl sulphoxide and dimethylformamide it is $Hg(SCN)_2 < Hg(SCN)_4^{2-} < HgCl_2 < HgBr_2 < HgI_2 < HgCl_4^{2-} < HgBr_4^{2-} < HgI_4^{2-}$.

In alcoholic mercury halide solutions the complexes $HgHal_3^-$ and $HgHal_4^{2-}$ predominate [154,156] (a situation analogous to that in aqueous solutions [174]), but their stability is low: in methanol $K_{st} = (1.10\text{–}1.86) \times 10^4$ for HgI_3^-. [152] The presence of only $HgBr_3^-$ with $\lg K_{st} = 3.3$ was noted in acetone [154,175]. The stability of mercury iodide solvato-complexes with alcohols and acetone decreases in the sequence methanol > propanol > butanol > hexanol > acetone [176].

The heats of formation of mercury iodide complexes in amides and sulphoxides are independent of the radius of the outer-sphere cation [159]: the complexes HgI_3^- and HgI_4^{2-} are very stable. The logarithms of their stability constants are respectively 30.4 and 32.6 in dimethyl sulphoxide [80] and 33.3 and 37.3 in dimethylformamide [39]. The formation of mercury halide and thiocyanate complexes in these solvents is accompanied by an exothermic heat change; the heats of formation of complexes having analogous compositions are higher in dimethylformamide than in dimethyl sulphoxide [160]. The complexes are particularly stable in acetonitrile, where the species HgL_3^-, HgL_4^{2-} and $Hg_2L_5^-$ exist [164].

2. The Stability Scales of Mercury Complexes

The interpretation of the measurements and comparison of the stabilities of the complex species in various solvents become possible when the concept of ionic activity is used; the quantities $p\gamma_t(Hg^{2+})$ constitute a basis for the construction of scales characterising the relative affinities of the ligands for Hg^{2+} ions; some of these pHg^{2+} scales are illustrated in Fig. 1. The scales are displaced relative to the stability scale for mercury complexes in water by $p\gamma_t(Hg^{2+})$; [62] the beginning of each scale corresponds to $[Hg(Solv)_m^{2+}] = 1$ M. The greater the downward displacement of the pHg^{2+} scale in a solvent (Solv) the greater the ability of solvent molecules to displace the ligands L^{l-} lying higher in this series from the inner coordination spheres of the complexes. The logarithms of the exchange equilibrium constants correspond to the distance between the corresponding "ligand donor–acceptor" pairs on the

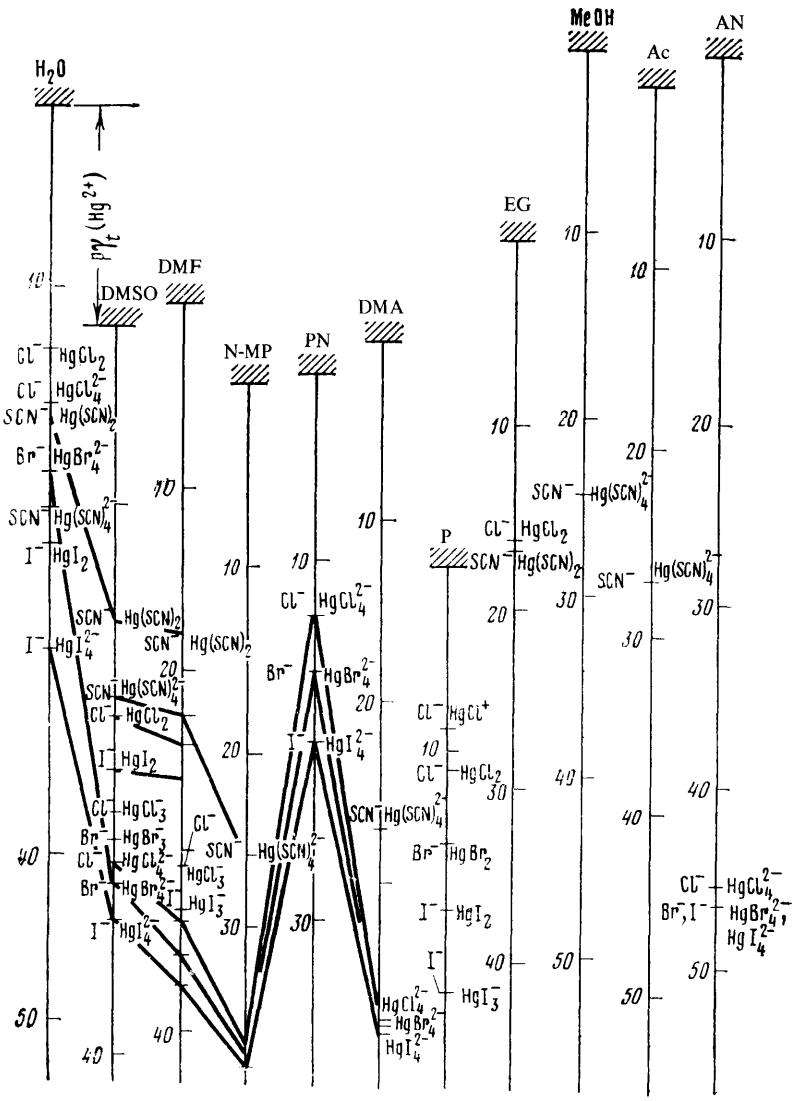


Figure 1. pHg^{2+} stability scales for mercury complexes in water and non-aqueous solvents. The designations of the solvents correspond to those in Table 1.

pHg^{2+} scale in terms of units of $\lg K$. Thus the reaction

$$HgCl_2 + 2SCN^- \overset{K}{\rightleftarrows} Hg(SCN)_2 + 2Cl^-$$

proceeds to the right in water ($\lg K = 3.6$), changes direction in dimethylformamide and dimethyl sulphoxide ($\lg K = -6.4$ and -5.1 respectively), and in *N*-methylpyrrolidone any halide displaces a thiocyanate ion from its mercury complex.

Evidently the removal of traces of water from solvents which weakly solvate Hg^{2+} cations (acetonitrile, nitromethane, and trifluoroacetic acid) is especially important: in aqueous acetonitrile mixtures water molecules occupy sites in the inner coordination sphere of the complex up to appreciable acetonitrile concentrations. On the other hand, the presence of even small amounts of amides in aqueous solutions of mercury compounds causes transolvation of the coordination sphere with replacement of water molecules (partial or complete) by the molecules of the organic cosolvent.

The positions of the complex species $[HgL_n]^{(2-nl)+}$ on the pHg^{2+} scale is determined by the solvation of all the species involved in the complex-formation reaction

$$p K^{Solv}_{[HgL_n]^{(2-nl)+}} = p K^{H_2O}_{[HgL_n]^{(2-nl)+}} + p\gamma_t(Hg^{2+}) + n \cdot p\gamma_t(L^{l-}) - p\gamma_t([HgL_n]^{(2-nl)+}). \quad (4)$$

Eqn. (4) has been used[54] to calculate the activity coefficients of mercury complexes. Aprotic dipolar solvents weakly solvate anionic complexes of mercury: for the chloride complex with the limiting coordination ($n = 4$), the values of $p\gamma_t$ are 8.8 in dimethylformamide, 7.7 in dimethyl sulphoxide, and 10.1 in dimethylacetamide. The weak solvation of cationic and molecular complexes of mercury in hydroxylated solvents leads to an increase of the activity of these complexes in reactions involving electrophilic addition to olefins.

The equation

$$pSP^{Solv}_{Hg_2L_2} = pSP^{H_2O}_{Hg_2L_2} + p\gamma_t(Hg_2^{2+}) + 2p\gamma_t(L^-) \quad (5)$$

for the solubility products of sparingly soluble mercury(I) compounds, which is analogous to Eqn. (4), makes it possible to calculate from the ionic activities and the known values of $SP_{Hg_2L_2}$ in water the solubilities of mercury(I) salts in non-aqueous solvents and to solve with the aid of Eqn. (3) the problem of the disproportionation of mercury halides in reference electrodes in measurements in non-aqueous media. Such calculations have demonstrated the absence of the disproportionation of sparingly soluble mercury(I) salts in the absence of an excess of ligands even in aprotic dipolar solvents. When there is an excess of ligands (which is typical for electrodes of the second kind) mercury halides are resistant to disproportionation in alcohols, formamide, and acetic acids [177].

3. Correlations in the Series of Mercury Complexes and Solvates

The experimental determination of the equilibrium constants for mercury systems in both water and non-aqueous solvents is complicated by solvolysis and disproportionation reactions. It is therefore of interest to follow the possibility of using methods of comparative calculation for predicting the stability of mercury(II) complexes and ionic activity coefficients.

The ratio of the constants for successive coordination stages. The successive equilibrium constants for individual stages involving many metal ion complexes with the same ligands usually decrease, as expected from an examination of statistical factors, steric effects, and Coulombic interaction [90]. According to Bjerrum [23,106], the stability of complexes corresponding to successive coordination stages is determined by the ratio

$$\frac{k_n}{k_{n+1}} = \frac{(N-n+1)(n+1)}{(N-n)\cdot n}, \quad (6)$$

where k_n and k_{n+1} are the stability constants of the nth and $(n+1)$th coordination stages and N is the maximum coordination number of the ion. However Eqn. (6) cannot fully characterise the stability of successively formed mercury(II) complex species: polarisation, statistical, and solvation effects are responsible for deviations of the experimental data from those calculated by the equation [92]

$$\frac{\lg K_n}{n} = \lg k_1 - \lambda(n-1). \quad (7)$$

The deviations are especially large for the second coordination stage in aqueous solutions and reach 1.9 lg K units [54]. This stage is characterised by a high stability of the complexes owing to the change in the structure of complex species in the course of their successive formation. Thus the complex $HgCl^+$ is a distorted tetrahedron with the mercury atom in the centre and the Cl^- ion and the three water molecules at the vertices; $HgCl_2$ is a flattened octahedron with chloride ions (in the *trans*-positions) and four water molecules (at the corners of the square) at the vertices; $HgCl_3^-$ is a distorted tetrahedron with a water molecule at a vertex; finally $HgCl_4^{2-}$ is a regular tetrahedron [178]. The highest exothermic heat change corresponds to the second coordination stage for mercury complexes in water. With increase of n, the degree of outer-sphere hydration of the complexes becomes more pronounced, which, when combined with structural changes, makes the heats of successive complex-formation stages less exothermic [178,179].

The dependence of $\lg K_n/n$ on n for mercury complexes in non-aqueous solvents is linear, which makes it possible to determine the approximate stability constants of the complexes HgL^+ in methanol, dimethylformamide, dimethyl sulphoxide, *N*-methylacetamide, and ammonia [54].

Relation between the electrochemical and spectroscopic manifestations of solvation. Numerous examples of the parallel variation of the electrochemical and spectroscopic characteristics of compounds have been described in the literature [180]. Indeed the oxidation-reduction potentials are proportional to the energies of the lowest unoccupied and highest occupied molecular orbitals and the long-wavelength absorption frequency in the electronic spectrum is equal to the difference between the energies of the two frontal mercury orbitals. In the series of mercury solvato-complexes there is [30,31,65] a linear correlation between the changes in the standard potential ΔE^0 (the half-wave potential $\Delta E_{1/2}$) and the solvatochromic effect; for protic and aprotic dipolar solvents, these relations are respectively

$$\Delta E^0 = -0.67(\Delta\lambda_{max}) + 6.33, \quad (8)$$

$$\Delta E_{1/2} = -2.20(\Delta\lambda_{max}) - 1.32. \quad (9)$$

The empirical Eqns. (8) and (9) can be used to predict certain spectroscopic properties on the basis of preliminary electrochemical measurements.

Correlations between the activity coefficients and properties of the solvents. The dependence of $\lg\gamma_t(Hg_n^{2+})$ on the reciprocals of the dielectric constant $1/\epsilon$ and the negative logarithms of the autoprotolysis constants pK_S of the solvents is usually non-linear [65]. The scatter of the points indicates an appreciable role of specific solvation: owing to the presence of unfilled 6*s* orbitals in mercury, there is a possibility of a donor–acceptor interaction of its ions with the lone electron pairs of solvent molecules. However, for solvents of the same type (aliphatic monohydric alcohols) distinct linear relations between $p\gamma_t(Hg_n^{2+})$ and $(1/\epsilon)pK_S$ are observed [29]. The dependence of $\lg\gamma_t(Hg_n^{2+})$ on the donor numbers DN of the solvents is linear [29] for $DN > 10$; the non-linearity of the relation in the region of low donor numbers can be attributed to ion association in media with low dielectric constants and low solvating capacity.

Correlation in the series of isoelectronic ions. The linearity of the relations between the enthalpies of complex formation by ions with isoelectronic structures and similar radii [101,106] suggests that the variation of the stabilities of the complexes is also linear. Such relations for mercury(II) and silver(I) ions in water, dimethyl sulphoxide, and dimethylformamide are described [54] by the equations

$$\lg K^{H_2O}_{AgX_2^-} = 0.67\lg K^{H_2O}_{HgX_2} - 4.7,$$

$$\lg K^{DMSO}_{AgX_2^-} = 0.57\lg K^{DMSO}_{HgX_2} - 0.75,$$

$$\lg K^{DMF}_{AgX_2^-} = 0.71\lg K^{DMF}_{HgX_2} - 0.52,$$

which can be used to estimate the stabilities of the molecular complexes of mercury from data for the analogous

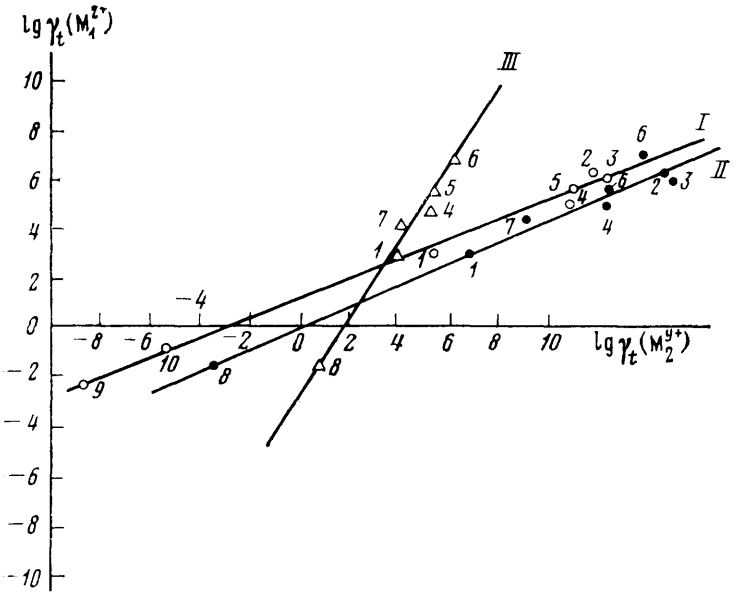


Figure 2. Dependence of $\lg\gamma_t(M_1^{z+})$ on $\lg\gamma_t(M_2^{y+})$ for ion pairs: I) Ag^+–Hg^{2+}; II) Ag^+–Hg_2^{2+}; III) Ag^+–Tl^+; solvent: 1) ethylene glycol; 2) pyrrolidone; 3) *N*-methylpyrrolidone; 4) dimethylformamide; 5) dimethylacetamide; 6) dimethyl sulphoxide; 7) *N*-methylacetamide; 8) propylene carbonate; 9) nitromethane; and 10) acetic acid.

silver complexes. Methods of comparative calculation can be used also for the approximate estimation of the activity coefficients for the transfer of Hg_n^{2+}, Ag^+, and Tl^+ ions. Some of these relations are illustrated in Fig. 2. The literature data are particularly numerous for silver ions; the use of relations analogous to those shown makes it possible to estimate not only the stability constants of the complexes and the ionic activity coefficients but also the stability constants of the solvato-complexes and the standard potentials of the mercury systems.

The results presented indicate an extremely vigorous development in recent years of the chemistry of mercury complexes. Apart from the wide-scale use of mercury compounds, this is associated with efforts directed towards the creation of a theory of solutions. With all the imperfection of the theoretical principles of non-aqueous titrimetry, there is no doubt that the use of quantitative characteristics of solvation processes (ionic activity coefficients) can serve as a reliable criterion for a well-founded choice of solvent. This approach to reactions involving the formation of mercury complexes leads to new possibilities, permitting the prediction of the equilibrium constants for reactions with participation of mercury compounds and the calculation of the activities of the reacting complex or simple forms of mercury.

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